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(71) Applicant (for all designated States except US): EAST-
MAN KODAK COMPANY [US/US]; 343 State Street,
Rochester, NY 14650 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): ROUSSILHE,
Jacques [FR/FR]; Kodak Industrie, Dépt. Brevets, CRT
- Zone Industrielle, F-71102 Chalon-sur-Saône Cedex

(FR). TSOI, Slu, Chung [GB/GB]; Kodak Limited,
Patent Dept., Headstone Drive, Harrow, Middlesex HA1
4TY (GB). HOFFMANN, Andrew, Francis [US/US];
Eastman Kodak Company, Patent Dept., 343 State Street,
Rochester, NY 14650 (US).

(74) Agent: HONORE, Anne-Claire; Kodak Industrie,
Dépt. Brevets, CTR - Zone Industrielle, F-71102
Chalon-sur-Saône Cedex (FR).

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(54) Title: DEVELOPER CONCENTRATE FOR BLACK AND WHITE DEVELOPMENT OF PHOTOGRAPHIC MATERIALS

(57) Abstract: The present invention relates to an aqueous developer concentrate for the black and white development of silver halide photographic materials, without hydroquinone, said developer concentrate having the advantage of remaining stable and not having a problem of precipitation during storage. The developer concentrate according to the invention comprises as main developer hydroquinonesulfonic acid or one of its salts, and as co-developer a mixture comprised of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and at least one substituted 3-pyrazolidone type co-developer.

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DEVELOPER CONCENTRATE FOR BLACK AND WHITE
DEVELOPMENT OF PHOTOGRAPHIC MATERIALS

FIELD OF THE INVENTION

The present invention relates to a new aqueous developer
5 concentrate for the black and white development of silver halide photographic materials.

BACKGROUND OF THE INVENTION

A developer can comprise different developing agents. Such
developing agents are described in Chimie et Physique photographiques, P.
10 Glafkides Chapter IX, pages 152-170, fifth edition. In general, a main developing agent is used in combination with an auxiliary developing agent. In some cases, a synergy effect is seen between the main developer and the auxiliary developer or "co-developer", i.e. the combined activity of the mixture of these two agents is greater than the sum of the activities of each of these agents used separately in the
15 same solution. This phenomena called "super-additivity" is explained by Mason in "Photographic Processing Chemistry", Focal Press, London, 1975.

Polyphenols, for example hydroquinone, and reductones, for example compounds of the ascorbic acid type, are the main developers most used in practice in black and white developing solutions.

20 Among the co-developers the most often used are aminophenols, like Elon[®] (methyl-p-aminophenol sulfate), 1-phenyl-3-pyrazolidones or Phenidones, such as Phenidone-A (1-phenyl-3 pyrazolidone), Phenidone-B (1-phenyl-4 methyl-3-pyrazolidone), Dimezone (1-phenyl-4,4'-dimethyl-3-pyrazolidone), Dimezone-S (1-phenyl-4-methyl-4'-hydroxymethyl-3-
25 pyrazolidone). Additional representative examples of aminophenols and phenidones are described in US Patents 2,688,549, 2,691,589, 3,865,591, 4,269,929 4,840,879 and 5,236,816, and in the article by G. B. Ficken and B. G. Sanderson, The Journal of Photographic Science, Vol., 1963, pages 157-164.

Photographic developers can be sold as working strength diluted
30 solutions or also be packaged as powders to be dissolved in water or concentrated liquids to be diluted before use. The packaging of a developer depends on the

solubility and stability of its various components and the user's preferences. The current trend is to reduce the number of components in kits and the volume of the packaging to reduce costs. One solution consists in the use of very concentrated developers, but these must then have great stability during storage.

5 Conventional 3-pyrazolidone type co-developers have the disadvantage of having insufficient solubility in water. Therefore, when 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone is used as co-developer in a developer concentrate, this developer concentrate can remain stable for a long time in a supersaturated state and then produce, by exposure to a low temperature or
10 possibly by other factors not yet identified, a precipitation of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone, making the developer concentrate unusable.

One solution would be to use an auxiliary solvent, of the diethylene glycol type. But this would cause an increase of the developer's bio-chemical
15 oxygen demand, and a cost increase, that is not acceptable.

Because of the poor solubility of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone, it is not feasible to manufacture a mono-component developer as a powder, which would be easily soluble in water at ambient temperature. A two-component developer as a powder has the disadvantage of
20 multiplying the packaging, increasing costs and reducing the ease of use.

Another solution to improve solubility consisted in introducing solubilizing groups into 3-pyrazolidone type compounds. The article of Zhurnal Nauchnoi i Prikladnoi Fotografii i Kinematografii 10, (5), 321-329 (1963) by V. L. Abritalin et al describes photographic developers comprising hydroquinone and a
25 number of 3-pyrazolidone derivatives of which some carry solubilizing groups directly attached to the benzene ring. But, according to this article, the introduction of carboxyl or sulfo solubilizing groups to the benzene cycle produces a large drop in super-additivity. This trend is also reported by G. E. Ficken and B. G. Sanderson in The Journal of Photographic Science, Vol. 11, 1963, pages 157-160,
30 who report that the introduction of a carboxylic group on phenidone reduces the super-additivity of the Phenidone/hydroquinone mixtures.

Hydroquinone based developers generally give good results, but have disadvantages for health and environmental protection. This is why ascorbic acid is used instead of hydroquinone in combination with phenidones in many developing compositions.

5 US-A-5,780,212 describes a developer comprising as main developer an ascorbic acid type compound and as co-developer new 3-pyrazolidone type compounds that have improved solubility. However, ascorbic acid type developers are sensitive to oxidation. Therefore it is necessary to adjust the development times, the geometry of processing tanks and the formulation of
10 developers to minimize oxidation and obtain sensitometric results comparable with those obtained with hydroquinone type developers. US-A-5,837,434 proposes the use of development accelerators to remedy these disadvantages.

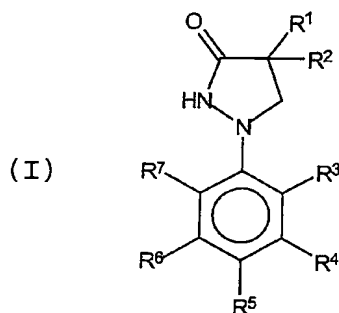
Hydroquinone can also be replaced by hydroquinonesulfonic acid or one of its salts. GB-A-2,329,973 describes a ready-to-use developer, containing
15 hydroquinonesulfonic acid as main developer and a co-developer that can be 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone. In order to obtain sensitometric results identical to those obtained with a developer using a hydroquinone/Métol® combination, it is necessary to add a development accelerator that is a polyglycol with average molecular weight between 200 g/mol and 600 g/mol. This document
20 does not mention other forms of use than the diluted working strength form and does not deal with the precipitation problem that can occur with development concentrates containing 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone.

SUMMARY OF THE INVENTION

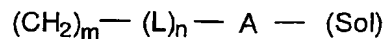
The present invention proposes an aqueous developer concentrate
25 provided as a single part that remains stable and does not have a precipitation problem during storage, and that enables a working strength developer to be obtained keeping a super-additivity effect similar to existing developers and enabling sensitometric results to be obtained comparable to those obtained with hydroquinone type developers for the same processing time without the need to
30 use a development accelerator.

The aqueous developer concentrate for black and white development according to the present invention is free of hydroquinone, comprises hydroquinonesulfonic acid or one of its salts as main developer, and is characterized in that

- 5 a) it comprises as co-developer a mixture comprised of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and at least one 3-pyrazolidone type co-developer of formula (I),
- b) the concentration of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone is lower than the solubility of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone measured at 18°C in a developer with composition similar to said developer concentrate but not comprising a co-developer, and
- 10 c) the quantity of 3-pyrazolidone type co-developers of formula (I) is between 2 and 60 mole percent in relation to the total quantity of co-developers, the 3-pyrazolidone type co-developer of formula (I) being:



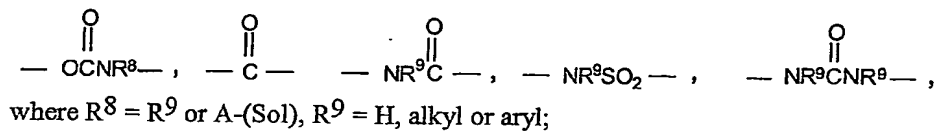
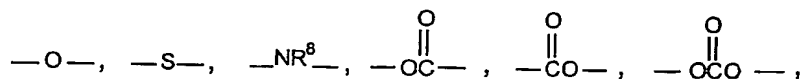
where R¹ and R² each independently represents hydrogen, a substituted or not substituted alkyl group, or a group having the formula:



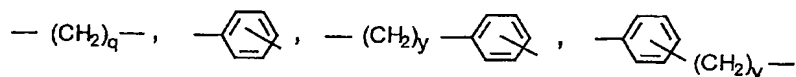
where m is between 0 and 5 and n is 0 or 1,

L represents a divalent group selected from among

5



A represents a divalent group selected from among

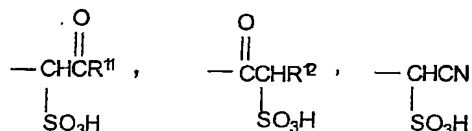


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where q is between 0 and 5, and y is between 1 and 3;

(Sol) is a solubilizing group selected from among:

CO_2H , SO_3H , SO_3K , $NHSO_2R^{10}$, SO_2NH_2 , SO_2NHR^{10} ,
polyhydroxyalkyl,

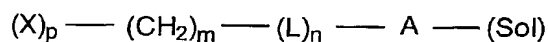


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where R^{10} is alkyl or aryl, R^{11} is OH, alkyl or aryl and R^{12} is hydrogen, alkyl or aryl;

R^3 to R^7 in formula (I) each independently represents hydrogen, an alkyl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryloxy group, or a group having the formula:

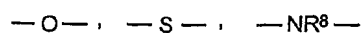
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where $p = 0$ or 1;

X represents a divalent group selected from among

20



m , L , n , A , (Sol) and R^8 are as defined above,

with the further proviso that at least one of the radicals R^1 to R^7 must contain a (Sol) group.

The present invention also relates to a working strength developing solution, obtainable by dilution of the developer concentrate described above.

5 The present invention also relates to a process for a black and white photographic development or for the black and white development step of color reversal films and papers comprising contacting an exposed photographic material with a working strength developing solution, obtainable by dilution of the developer concentrate described above.

10 The developer concentrate according to the present invention and its working strength solution can be used to develop black and white materials, like graphic arts materials, x-ray materials, black and white photographic films and papers, microfilms or for the black and white development step of color reversal films and papers.

15 **BRIEF DESCRIPTION OF THE INVENTION**

Figures 1 and 2 represent the sensitometric curves obtained with control developers and with developers according to the present invention used for the black and white development step of color reversal films.

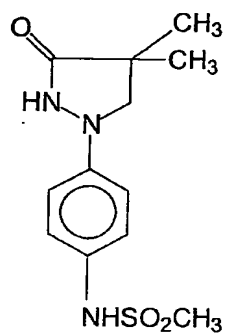
DETAILED DESCRIPTION OF THE INVENTION

20 The aqueous developer concentrate according to the present invention comprises hydroquinonesulfonic acid or one of its salts as main developer of silver halides. Preferably, potassium hydroquinone-monosulfonate is used.

25 The co-developer comprises a mixture of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and a 3-pyrazolidone type co-developer of formula (I) as defined above. These co-developers of formula (I) have solubilizing groups that are generally not directly attached to the phenyl ring or pyrazolidino ring and are described in Patents US-A-5,780,212 and US-A-5,942,379.

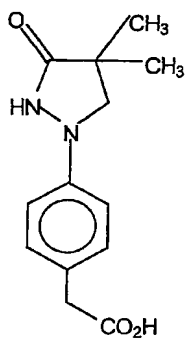
30 Examples of 3-pyrazolidone type compounds of formula (I) useful in the present invention have the following formulas:

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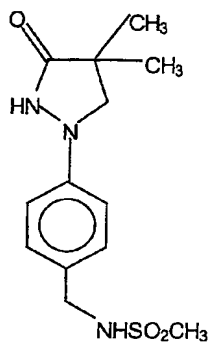


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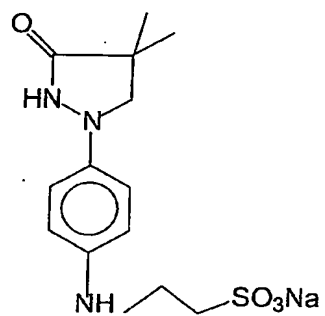
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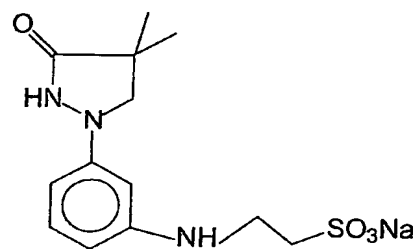
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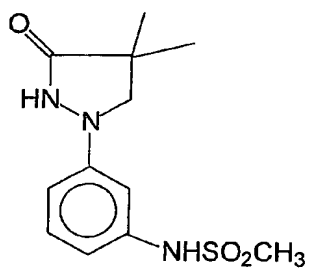


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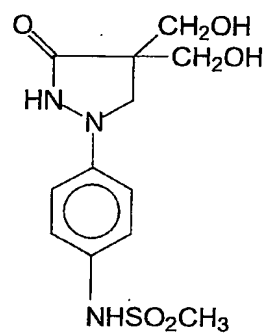


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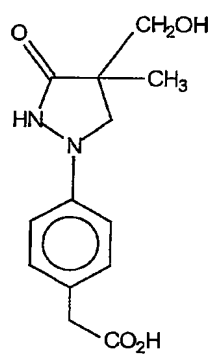
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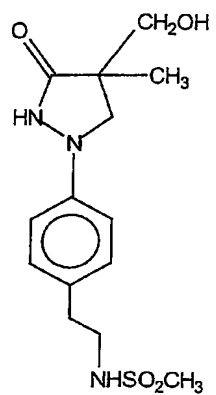
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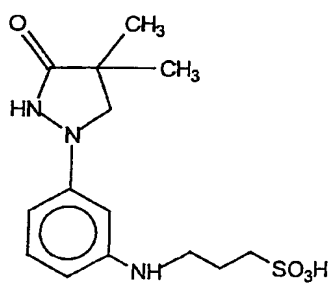
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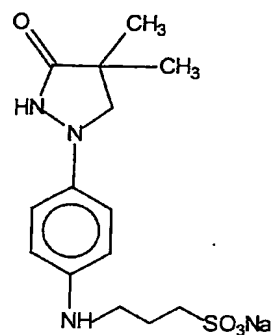
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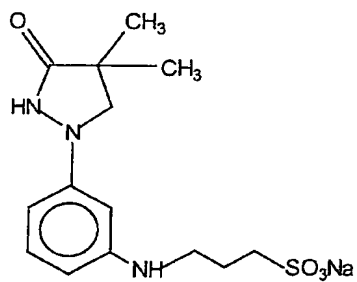
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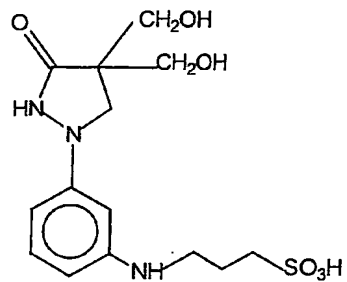
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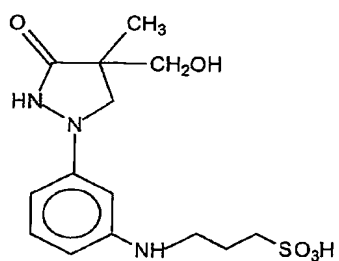
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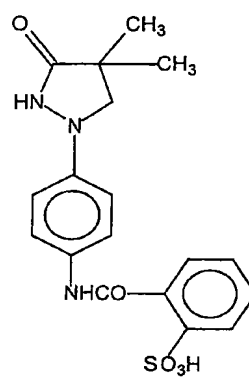
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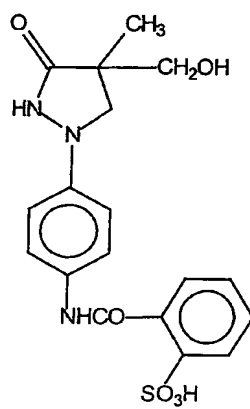


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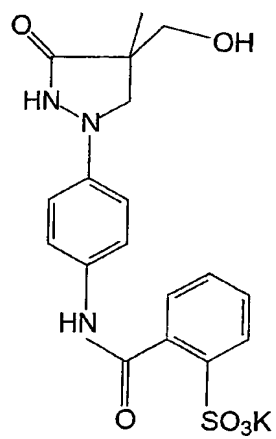


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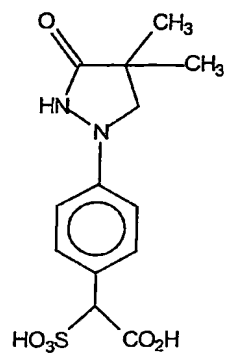


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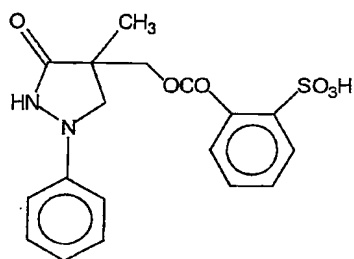
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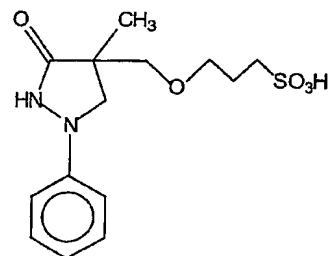
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3-pyrazolidone type compounds (1) and (17) are especially preferred.

5 Other 3-pyrazolidone type compounds useful in the present invention have the following formulas:

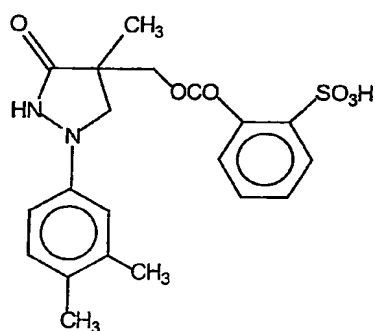


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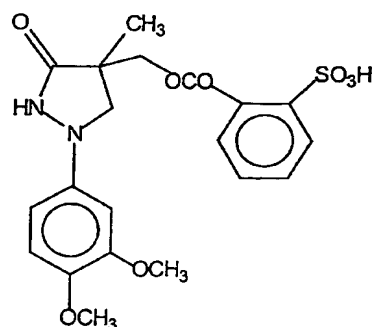


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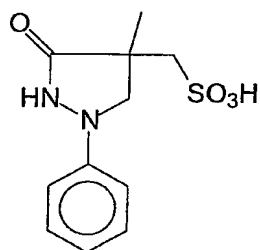
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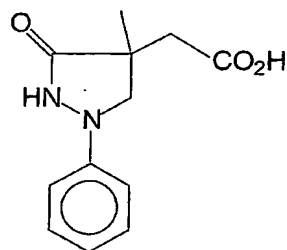
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(24)

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In the developer concentrate, the concentration of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone is lower than the solubility of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone measured at 18°C in a developer with composition similar to said developer concentrate but not initially comprising a co-developer. This solubility was measured by adding 1 gram of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone to 100 ml of tested developer concentrate. The sample was kept at 18°C and was stirred daily. After one week, the sample was filtered using a 3 µm filter. The supernatant was analyzed by chromatography.

15

In the developer concentrate according to the invention, the concentration of main developer of hydroquinonesulfonic acid type is between 50

g/l and 150 g/l, and preferably between 80 g/l and 120 g/l and the weight ratio of main developer to 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone is preferably greater than 10 to ensure complete efficiency of the working strength developer.

5 The quantity of 3-pyrazolidone type co-developers of formula (I) is between 2 and 60 mole percent in relation to the total quantity of co-developers. One or more 3-pyrazolidone type co-developers of formula (I) can be used in combination with 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone.

 In addition to the main developer and the co-developer, the
10 developer concentrate according to the invention can contain numerous conventional additives such as an antioxidant, a sequestering agent, a buffering agent, an antifoggant, a solvent, a surfactant, anti-sludging agents, contrast-promoting agents, halides (such as iodide and bromide salts), a silver metal solvent (such as thiocyanates), and other additives known to those skilled in the art.

15 The antioxidant can be sulfite or a compound capable of supplying sulfite ions in aqueous solution. The antioxidant can be a sulfite, a bisulfite, or a metabisulfite. For example, alkali metal or ammonia salts, such as sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium, potassium or ammonium metabisulfite can be used.

20 The buffering agent or a compound capable of controlling the pH can be for example a carbonate, a bicarbonate boric acid or a boric acid salt, or an alkanolamine.

 Sequestering agents, especially to trap calcium and magnesium
ions, can be polyphosphonic acids and aminopolycarboxylic acids and salts
25 thereof.

 In the scope of the invention, the composition of the developer concentrate is capable of numerous variants accessible to those skilled in the art according to the planned application.

 The developer concentrate according to the present invention is
30 diluted with water to obtain a working strength solution, just before its use. The developer concentrate according to the invention can be diluted up to 10 times

with water. Dilution between 5 and 6 times is preferred. The working strength developing solution then preferably comprises between 15 g/l and 25 g/l of hydroquinonesulfonic acid or one of its salts as main developer, between 0.5 g/l and 2 g/l of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and between 0.5 g/l and 2 g/l of 3-pyrazolidone type co-developer of formula (I).

The developer concentrate according to the present invention comprises a quantity of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone selected to be lower than the solubility of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone in the developer concentrate and to no longer be in supersaturation condition to no longer have a precipitation problem. Surprisingly, the combination of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone with 3-pyrazolidone type co-developers of formula (I) and a hydroquinonesulfonic acid type main developer enables a working strength developer to be obtained keeping a super-additivity effect and enabling sensitometric results to be obtained comparable with those obtained with known hydroquinone based developers, without the need to add development accelerators.

The invention is illustrated by the following examples:

Example 1

Synthesis of the compound [4-[4,4'-dimethyl-3-oxo-1-pyrazolidinyl]phenyl]amino methanesulfonyl (Compound (1))

To a solution of p-nitrophenylhydrazine (2g, 13.1 mol) in dry pyridine (20 ml) was added dropwise 3-chloropivaloyl chloride (2.43 g, 15.7 mmol) at 5°C under nitrogen. The reaction mixture was held at 5°C for two hours and then it was heated to reflux under nitrogen for 20 hours. The mixture was then cooled to ambient temperature and then poured into a water/ice (200 ml) and concentrated HCl (20 ml) mixture with rapid stirring. A yellow solid was collected by suction filtration, which was washed with water, then dried under vacuum on phosphorous pentoxide. 2.02 g (66%) of [4-[4,4'-dimethyl-3-oxo-1-pyrazolidinyl]nitrobenzene was obtained as a yellow solid.

A mixture of this product (2 g, 8.51 mmol) and palladium carbon (0.1 g, 10% Pd) in tetrahydrofuran (250 ml) was hydrogenated under 29

atmospheres of hydrogen at ambient temperature for 20 hours. The catalyst was removed by filtration; the filtrate was stirred under nitrogen and a mixture of triethylamine (2.15g, 21.3 mmol) and N,N-dimethylaminopyridine (10 mg) was added. Methanesulfonyl chloride (1.07g, 9.36 mmol) was then added dropwise and then stirred at ambient temperature for 20 hours. This solution was concentrated under reduced pressure and then poured into a water/ice (250 ml) and concentrated HCl (10 ml) mixture with stirring. The resulting mixture was extracted with ethyl acetate (3 x 100 ml), washed with brine (2 x 100 ml) and then dried on magnesium sulfate. The solvent was removed under reduced pressure to obtain a yellow solid. The crude product was recrystallized from acetonitrile then dried under vacuum. 1.4 g (58%) of compound (1) was obtained as a pale pink solid.

Example 2

Synthesis of the compound 2-[[[4-[4-(hydroxymethyl)-4-methyl-3-oxo-1-pyrazolidinyl]phenyl]amino]carbonyl]benzenesulfonic acid, potassium salt (compound (17))

- a) 2,2-bis(hydroxymethyl)propionic acid (67 g, 0.5 mol) was added to thionyl chloride (138 ml, 1.9 mol) at ambient temperature and then heated to reflux for 4 hours with stirring. A clear colorless solution was obtained that was cooled to ambient temperature, then the excess thionyl chloride was removed under reduced pressure. A pale yellow liquid was obtained. The crude product was purified by vacuum distillation to give 84.2 g (85%) of compound (a) as a clear colorless liquid.
- b) To a solution of 4-nitrophenylhydrazine (136.4 g, 0.892 mol) in dry pyridine (500 ml) were added dropwise the compound (a) (177.1 g, 0.892 mol) and hydrochloric acid at 5°C under nitrogen and with stirring. The addition rate was such that the internal temperature was held below 10°C. When the addition was finished, the mixture was stirred at 5°C for 1 hour, then at ambient temperature for 1 hour and then at 95°C for 2.5 hours. The resulting mixture was cooled, poured

into a 15% solution of HCl (6 l) with stirring, then stirred for one hour. A yellow solid was collected by suction filtration, which was washed with water (3 l) then dried under vacuum on phosphorous pentoxide. 189.6 g (84.7%) of compound (b) was obtained as a yellow-orange powder.

- 5 c) A mixture of this compound (b) (40 g, 0.16 mmol) and palladium carbon (3.2 g, 10% Pd) in tetrahydrofuran (400 ml) was hydrogenated under 30 atmospheres of hydrogen at 45°C for four hours and then at ambient temperature for 24 hours. The catalyst was filtered and the solvent removed under reduced pressure. Compound (c) was obtained as a green sludge. This crude product (c)
10 was used immediately for the following reaction without further purification.
- d) 0.16 mol of compound (c) were dissolved in acetonitrile (400 ml). A greenish solution was obtained. A solution of cyclic anhydride of 2-sulfobenzoic acid (14.7 g, 0.08 mol) in acetonitrile (60 ml) was added dropwise with rapid stirring. A precipitate formed immediately. Triethylamine (8 g, 0.08 mol) was
15 added and the precipitate disappeared to give a blue solution. Other additions were performed in the following manner:

7.4 g anhydride in 30 ml acetonitrile and 4 g triethylamine

3.7 g anhydride in 20 ml acetonitrile and 2 g triethylamine

1.85 g anhydride in 10 ml acetonitrile and 1 g triethylamine

20 1.85 g anhydride in 10 ml acetonitrile and 1 g triethylamine

1.85 g anhydride in 10 ml acetonitrile and 1 g triethylamine

- After these additions, a pink solution was obtained with a slightly sticky green deposit. The pink solution was separated from the deposit by settling and stirred at ambient temperature. A white precipitate formed immediately. The suspension
25 was stirred overnight at ambient temperature. The product was collected by suction filtration, washed with acetonitrile then dried under vacuum. 48 g (59.6 %) of triethylamine 2-[[[4-[4-(hydroxymethyl)-4-methyl-3-oxo-1-pyrazolidinyl]phenyl]amino]carbonyl] benzenesulfonic acid was obtained as a white solid (compound (d)).

- 30 e) DMSO was degassed by nitrogen bubbling for about 20 minutes. To a solution of the compound (d) (7.95 g, 15.71 mmol) in degassed DMSO (35 ml)

- was added potassium t-butoxide (1.8 g, 16 mmol) at ambient temperature, under nitrogen and with stirring. The solution was stirred under nitrogen at ambient temperature for 3.5 hours, then added dropwise to tetrahydrofuran (about 800 ml) with rapid stirring. A red/brown precipitate was recovered, which was suction
- 5 washed with THF using a sintered glass funnel. The solid was quickly transferred to a recrystallising dish while it was still damp with THF. Then the solid was dried in a vacuum dryer on phosphorous pentoxide. 6.07 g (87%) of potassium salt of 2-[[[4-[4-(hydroxymethyl)-4-methyl-3-oxo-1-pyrazolidinyl]phenyl]amino]carbonyl] benzenesulfonic acid (compound (17)) was obtained as a reddish hygroscopic
- 10 solid.

Examples 3-4

- In these examples, a Kodak Ektachrome 100 ® film was processed according to the Ektachrome E-6® process. This process is described in the manual Z-119 "*Using KODAK Chemicals, Process E-6*", Fifth Edition, published
- 15 by the Eastman Kodak Company. This process comprises different successive steps in different baths. In particular, the first bath corresponds to the first black and white development, this step being performed at 38°C for 6 minutes. For the first black and white development, the control developer (example 3) and the working strength developing solution according to the invention (example 4),
- 20 both obtained from developer concentrates whose composition is given in table I below, were used respectively. According to these compositions, the co-developer used in the developer concentrate according to the invention comprised 66.66-mol % of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and 33.33-mol % of compound (1). For one liter of working strength solution, 190 ml of corresponding
- 25 developer concentrate were used diluted with the required amount of water. The pH of working strength solutions was 9.68.

Table I

| Component | Example 3: control | Example 4: invention |
|------------------------------------|--------------------|----------------------|
| K ₂ SO ₃ 45% | 227 ml/l | 227 ml/l |
| NaSCN | 5 g/l | 5 g/l |
| NaBr | 7 g/l | 7 g/l |
| KOH 50% | 43 g/l | 43 g/l |
| Dequest ® 2000 ⁽¹⁾ | 4 g/l | 4 g/l |
| NaOH 50% | 2 ml/l | 2 ml/l |
| Versenex ® 80 ⁽²⁾ | 31 g/l | 31 g/l |
| HMMP ⁽³⁾ | 7.5 g/l | 5 g/l |
| Compound (1) | - | 3.4 g/l |
| K ₂ CO ₃ | 140 g/l | 140 g/l |
| NaHCO ₃ | 60 g/l | 60 g/l |
| KHQ S ⁽⁴⁾ | 117 g/l | 117 g/l |

(1) nitrilotris(methylene)trisphosphonic acid

(2) pentasodic salt of diethyltriaminepentaacetic acid

5 (3) 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone

(4) potassium hydroquinone-monosulfonate

After complete processing of the film, the sensitometric results obtained were compared. Figure 1 gives the sensitometric curves obtained using, for the first black and white development, the control developer and the developing solution respectively corresponding to examples 3 and 4 for 6 minutes of development. It can be seen that when the developer solution obtained from the developer concentrate according to the invention was used, sensitometric results comparable with the control developer were obtained, for the same processing time. The combination of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone with the compound (1) as co-developers and potassium hydroquinone-monosulfonate as main developer enabled a working strength developer to be obtained keeping the same super-additivity effect as the known control developer.

Further, the solubility of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone in the developer concentrate was measured by adding 1 gram of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone to 100 ml of a developer concentrate with composition similar to example 3 but not initially comprising 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone. The sample was kept at 18°C and was stirred daily. After one week, the sample was filtered using a 3 µm filter. The supernatant was analyzed by chromatography. For the 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone a solubility of about 5.4 g/l at 18°C was measured. In the developer concentrate according to the invention (example 4), the concentration of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone was only 5 g/l, and thus lower than its solubility. Thus 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone in the developer concentrate according to the invention was no longer in supersaturation condition. During storage, the developer concentrate according to the invention does not have a problem of precipitation of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone.

Examples 5-6

In these examples, a Kodak Ektachrome 100S Professional® film was processed according to the Ektachrome E-6® process, using for the first black and white development working strength developing solutions obtained from the developer concentrates whose composition is given in table II below. According to these compositions, the co-developer used in the developer concentrate according to the invention comprised 55-mol % of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and 45-mol % of compound (17). For one liter of working strength solution, 190 ml of corresponding developer concentrate were used diluted with the required amount of water. The pH of working strength solutions was 9.83.

Table II

| Component | Example 5: control | Example 6: invention |
|-------------------------------------|--------------------|----------------------|
| K ₂ SO ₃ 45% | 324 ml/l | 324 ml/l |
| NaSCN 51% | 10.3 g/l | 10.3 g/l |
| NaBr | 14 g/l | 14 g/l |
| KOH 45% | 52 g/l | 52 g/l |
| Dequest ® 2006 ⁽¹⁾ , 40% | 7.4 g/l | 7.4 g/l |
| DTPA.5Na ⁽²⁾ , 40% | 33 g/l | 33 g/l |
| HMMP ⁽³⁾ | 6 g/l | 3.8 g/l |
| Compound (17) | - | 6.5 g/l |
| K ₂ CO ₃ | 73.5 g/l | 73.5 g/l |
| NaHCO ₃ | 53 g/l | 53 g/l |
| KHQS ⁽⁴⁾ | 97 g/l | 97 g/l |

(1) pentasodic salt of nitrilotris(methylene)trisphosphonic acid

(2) pentasodic salt of diethyltriaminepentaacetic acid

5 (3) 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone

(4) potassium hydroquinone-monosulfonate

After complete processing of the film, the sensitometric results obtained were compared. Figure 2 gives the sensitometric curves obtained using, for the first black and white development, the control developer and the developing solution respectively corresponding to examples 5 and 6 for 6 minutes of development. It can be seen that when the developing solution obtained from the developer concentrate according to the invention was used, sensitometric results comparable with the control developer were obtained, for the same processing time.

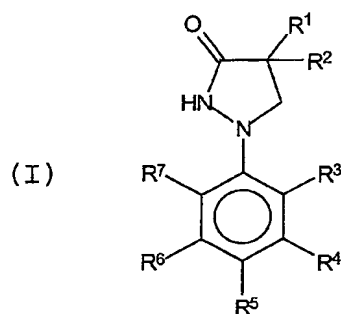
The combination of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone with the compound (17) as co-developers and potassium hydroquinone-monosulfonate as main developer enabled a working strength

developer to be obtained keeping the same super-additivity effect as the known control developer.

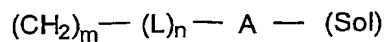
Furthermore, the solubility of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone in a developer concentrate with composition similar to example 5 but not initially comprising 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone was measured at about 6.1 g/l at 18°C. In the developer concentrate according to the invention, the concentration of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone was only 3.8 g/l, and thus lower than its solubility. Thus 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone in the developer concentrate according to the invention was no longer in supersaturation condition. During storage, the developer concentrate according to the invention does not have a problem of precipitation of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone.

WHAT IS CLAIMED IS

1. An aqueous developer concentrate for the black and white development of silver halide photographic materials, without hydroquinone, comprising hydroquinonesulfonic acid or one of its salts as main developer of silver halides, characterized in that
- a) it comprises as co-developer a mixture comprised of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and at least one 3-pyrazolidone type co-developer of formula (I),
 - b) the concentration of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone being lower than the solubility of 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone measured at 18°C in a developer with composition similar to said developer concentrate but not comprising a co-developer, and
 - c) the quantity of 3-pyrazolidone type co-developers of formula (I) being between 2 and 60 mole percent in relation to the total quantity of co-developers, the 3-pyrazolidone type co-developer of formula (I) being:



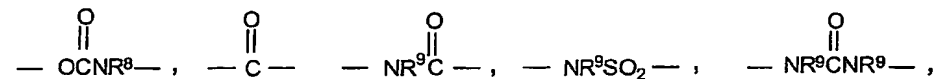
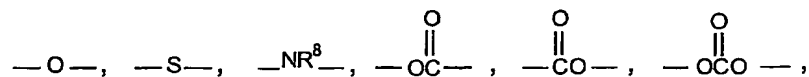
where R^1 and R^2 each independently represents hydrogen, a substituted or unsubstituted alkyl group, or a group represented by the formula:



where m is between 0 and 5 and n is 0 or 1,

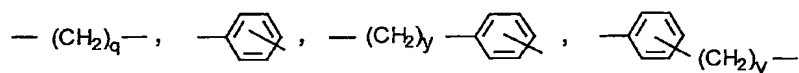
L represents a divalent group selected from among

23



where $\text{R}^8 = \text{R}^9$ or A-(Sol), $\text{R}^9 = \text{H}$, alkyl or aryl;

A represents a divalent group selected from among

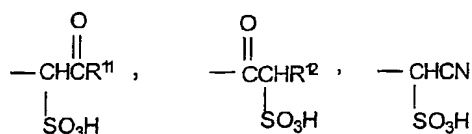


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where q is between 0 and 5, and y is between 1 and 3;

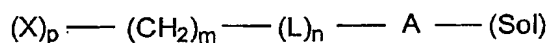
(Sol) is a solubilizing group selected from among:

CO_2H , SO_3H , SO_3K , $\text{NHSO}_2\text{R}^{10}$, SO_2NH_2 , $\text{SO}_2\text{NHR}^{10}$, polyhydroxyalkyl,



10 where R^{10} is alkyl or aryl, R^{11} is OH, alkyl or aryl and R^{12} is hydrogen, alkyl or aryl;

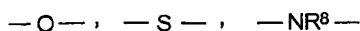
R^3 to R^7 in formula (I) each independently represents hydrogen, an alkyl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryloxy group, or a group represented by the formula:



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where $p = 0$ or 1 ;

X represents a divalent group selected from among



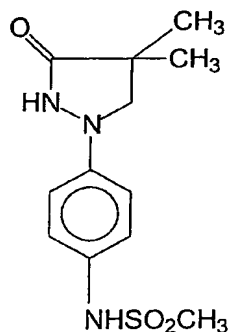
m , L , n , A , (Sol) and R^8 are as defined above

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with the further proviso that at least one of the radicals R^1 to R^7 must contain a (Sol) group.

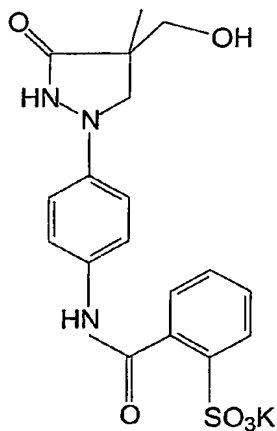
2. The developer concentrate of claim 1, wherein the main developer is potassium hydroquinone-monosulfonate.

5 3. The developer concentrate of claim 1, wherein the co-developer (I) is



4. The developer concentrate of claim 1, wherein the co-developer (I) is

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5. A working strength developing solution obtainable by dilution of the developer concentrate according to Claim 1.

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6. A photographic development method comprising contacting an exposed photographic material with a developer solution capable obtainable by dilution of the developer concentrate according to Claim 1.

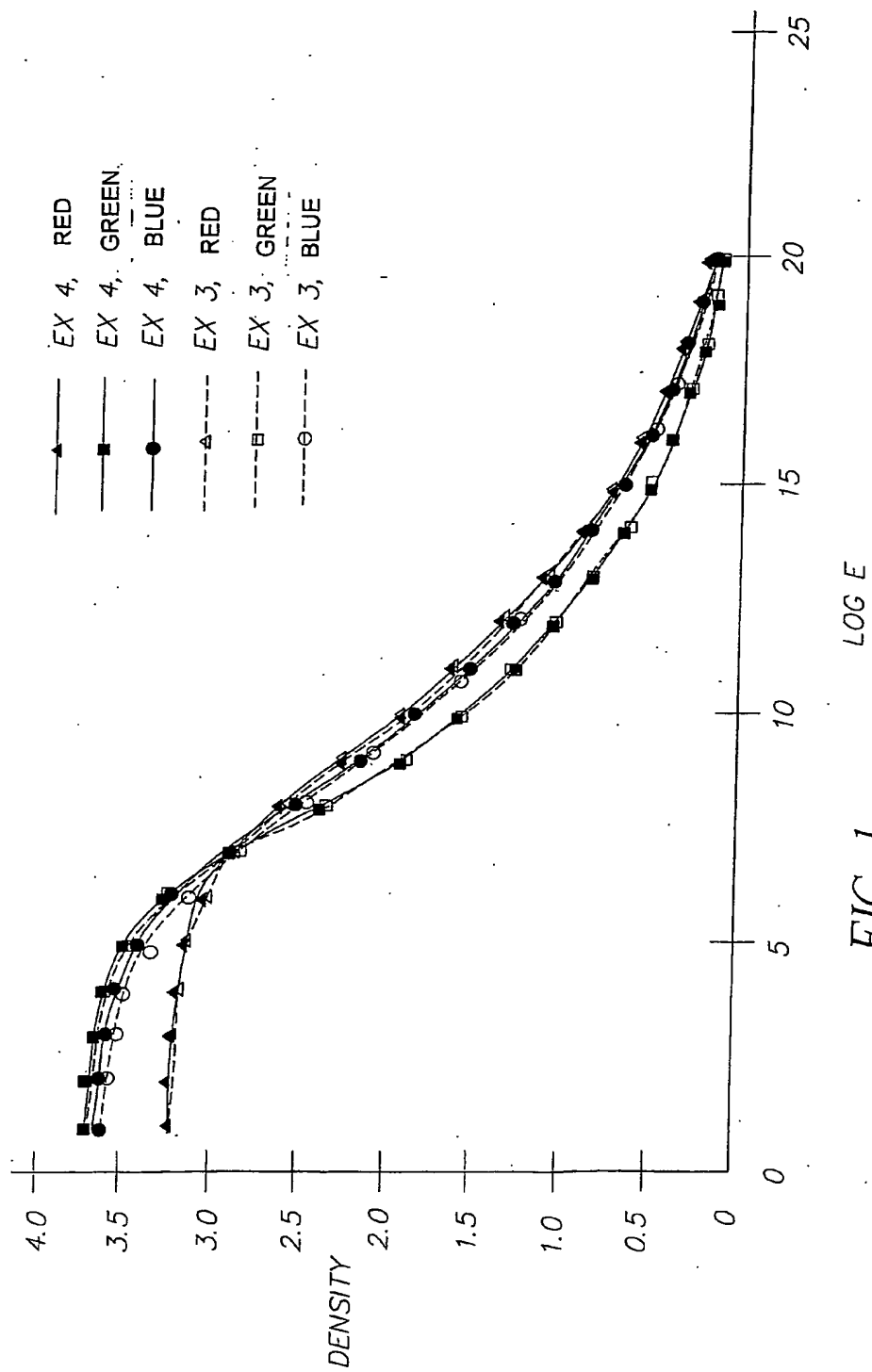


FIG. 1

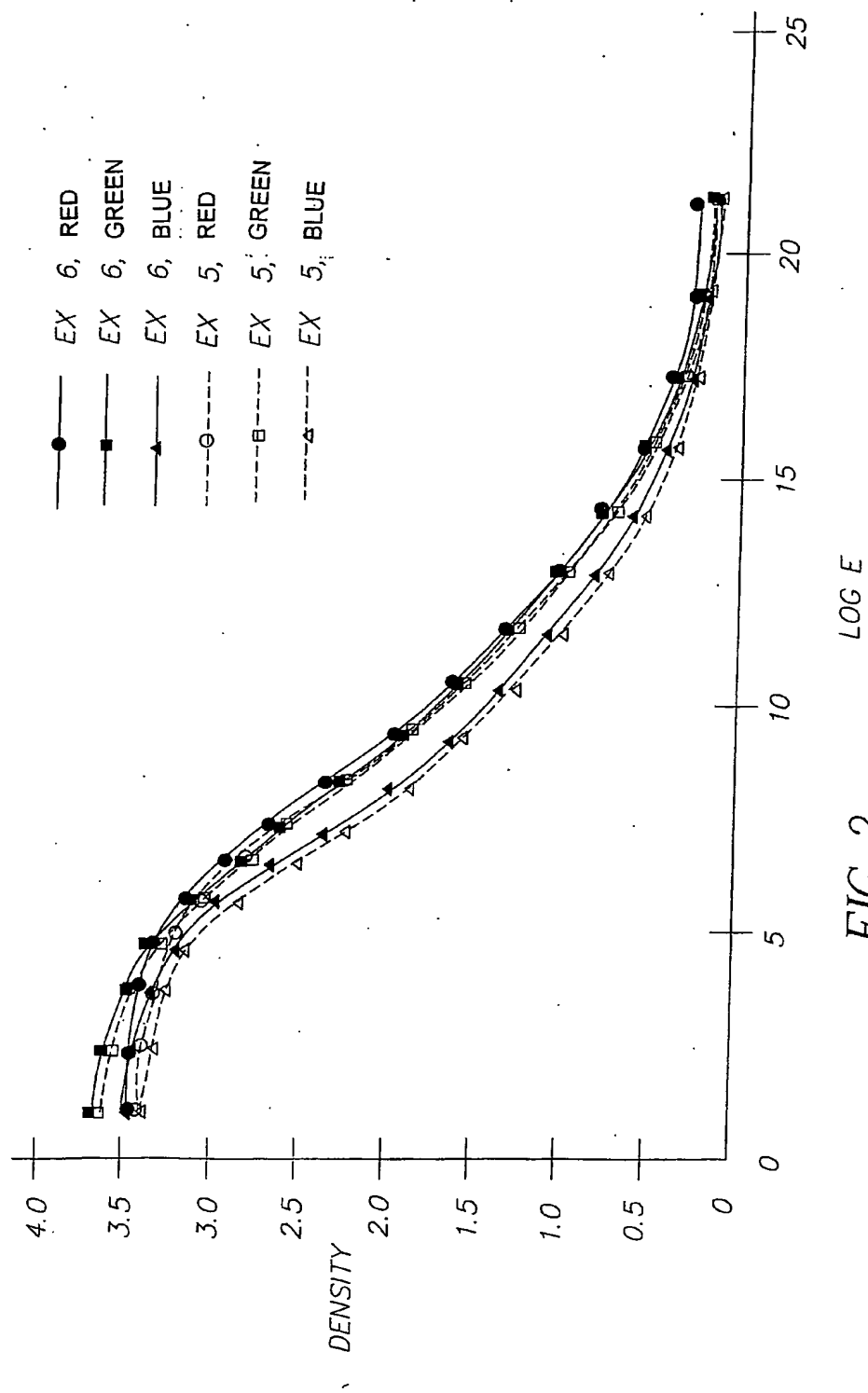


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/06007

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G03C5/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| Y | US 6 083 673 A (ROUSSILHE ET AL.) 4 July 2000 (2000-07-04) column 1, line 15 - line 17 column 1, line 66 - column 3, line 48 column 6, line 35 - line 46 column 7, line 43 - line 50 column 9, line 11 - line 25 | 1-3, 5, 6 |
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 July 2003

Date of mailing of the international search report

04/08/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application

PCT/EP 03/06007

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
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